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Document Name: Claims

1. A surface treatment agent comprising a fluorine-containing polymer and water and/or an organic solvent, characterized in that the fluorine-containing polymer comprises repeating units derived from a fluorine-containing monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

[wherein X is a hydrogen atom or a methyl group;
Y is -O- or -NH-;
Z is -S- or $-SO_2-$;
Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and
m is from 1 to 10, n is from 0 to 10, and p is 0 or 1].

2. The surface treatment agent according to claim 1, which is in the form of a solution, an emulsion or an aerosol.

3. A method of treating a subject material with the surface treatment agent defined in claim 1.

4. The method according to claim 3, wherein the subject material is a textile, a masonry, a filter (for example, an electrostatic filter), a dust protective mask, a fuel cell, glass, paper, wood, leather, fur, asbestos, brick, cement, a metal and oxide, a ceramic, plastics, a coated surface or a plaster.

5. A textile treated with the surface treatment agent defined in claim 1.

6. A carpet treated with the surface treatment agent

defined in claim 1.

7. A fluorine-containing monomer (a) of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

[wherein X is a hydrogen atom or a methyl group;
Y is -O- or -NH-;
Z is -S-;
Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and
m is from 1 to 10, n is from 0 to 10, and p is 0 or 1, provided that, when p is 0, Y is -NH-, and that, when p is 1, Y is -O- and n is 0].

8. The fluorine-containing monomer according to claim 7, wherein the number of carbon atoms in the fluoroalkyl group (Rf group) is from 1 to 4.

9. The fluorine-containing monomer according to claim 7, wherein the fluoroalkyl group (Rf group) is a perfluoroalkyl group.

10. A fluorine-containing polymer comprising (A) repeating units derived from the fluorine-containing monomer (a) defined in claim 7.

11. The fluorine-containing polymer according to claim 10, which further comprising
(B) repeating units derived from a monomer (b) free from a fluorine atom, and
(C) optionally, repeating units derived from a crosslinkable monomer (c),
in addition to the repeating units (A).

12. The fluorine-containing polymer according to claim 11, wherein the fluorine atom-free monomer (b) forming the repeating unit (B) is an acrylate of the general formula:

$CH_2=CA^1COOA^2$

[wherein A^1 is a hydrogen atom or a methyl group, and A^2 is a hydrocarbon group having 1 to 30 carbon atoms (particularly an alkyl group represented by C_nH_{2n+1} (n = 1 to 30))].

13. The fluorine-containing polymer according to claim 11, wherein the crosslinkable monomer (c) forming the repeating unit (C) is a fluorine-free monomer having at least two reactive groups and/or carbon-carbon double bonds.

14. The fluorine-containing polymer according to claim 11, wherein the amount of the fluorine atom-free monomer (b) is 0.1 to 50 parts by weight, and the amount of the crosslinkable monomer (c) is at most 20 parts by weight, based on 100 parts by weight of the fluorine-containing monomer (a).

Document Name: Specification

Title of the Invention: Surface Treatment Agent, Fluorine-Containing Monomer, and Fluorine-Containing Polymer

Technical Field

[0001]

The present invention relates to a polymer which imparts excellent water repellency, oil repellency and antifouling property to a textile, a masonry, an electrostatic filter, a dust protective mask and components of fuel cell, and treatments of such materials.

Background Art

[0002]

Hitherto, various fluorine-containing compounds have been proposed. The fluorine-containing compounds advantageously have properties excellent in heat resistance, oxidation resistance, weather resistance and the like. The fluorine-containing compounds are used, for example, as water- and oil-repellents and soil release agent because of their low free energies, i.e., their difficulty to adhere.

[0003]

As the fluorine-containing compound usable as a water- and oil-repellent, there is exemplified a fluorine-containing polymer which comprises (meth)acrylate ester having a fluoroalkyl group as a constituent monomer. The use of a (meth)acrylate ester having an organic group as a spacer between an acrylic acid group and a fluoroalkyl group, in the fluorine-containing polymer is proposed. Such fluorine-containing polymers having spacers are disclosed in, for example, US Patent No. 3655732, US Patent No. 3773826, US Patent No. 3916053 and US Patent No.

5439998. These fluorine-containing polymers, however, can not impart sufficient water- and oil-repellency.

[0004]

Various recent research results indicate that in view of the practical treatment of fibers with the surface treatment agents (particularly water- and oil-repellents), the important surface property is not a static contact angle, but is a dynamic contact angle, particularly a back contact angle. That is, the advance contact angle of water is not dependent on the number of carbon atoms in the side chain of a fluoroalkyl group, but the back contact angle of water is remarkably small when the number of carbon atoms in the side chain is 7 or less, as compared with the back contact angle of water when the number of carbon atoms therein is 8 or more. In correspondence to the contact angle, X ray analyses reveal that the side chain crystallizes when the number of carbon atoms in the side chain is 7 or more. It is known that the actual water repellency has correlation with the crystallization of the side chain and that the mobility of the molecule of the surface treatment agent is an important factor for exhibition of the actual performances (for example, MAEKAWA Takashige, FINE CHEMICAL, Vol. 23, No. 6, page 12 (1994)). Accordingly, it is considered that an acrylate polymer which has a short fluoroalkyl group of which the side chain has 7 or less carbon atoms (particularly 6 or less carbon atoms) can not exhibit practical performance (particularly water repellency) because of the low crystallinity at its side chain.

[0005]

JP-A-63-90588, JP-A-63-99285 and JP-A-01-315471

disclose that a fluorine-containing acrylate polymer in which the alpha-position is substituted with fluorine, chlorine or the like has excellent properties such as good adhesion to a substrate, high film strength and good water- and oil-repellency. It is also described in these publications that the fluoroalkyl group used in Examples has at least 8 carbon atoms; and the use of an acrylate monomer which has a fluoroalkyl group having 6 or less carbon atoms is not described in any of these publications.

[0006]

Results of recent studies (EPA Report "PRELIMINARY RISK ASSESSMENT OF THE DEVELOPMENTAL TOXICITY ASSOCIATED WITH EXPOSURE TO PERFLUOROOCTANOIC ACID AND ITS SALTS" (http://www.epa.gov/opptintr/pfoa/pfoara.pdf)), etc. reveal that PFOA (perfluorooctanoic acid) is a potential risky burden on the environmental. EPA (Environmental Protection Agency of USA) announced on April 14, 2003 that the EPA should vigorously make scientific investigation on PFOA.

On the other hand, Federal Register (FR Vol. 68, No. 73/April 16, 2003 [FRL-2303-8]) (http://www.epa.gov/opptintr/pfoa/pfoafr.pdf), EPA Environmental News FOR RELEASE: MONDAY APRIL, 2003 "EPA INTENSIFIES SCIENTIFIC INVESTIGATION OF A CHEMICAL PROCESSING AID" (http://www.epa.gov/opptintr/pfoa/pfoaprs.pdf), and EPA OPPT FACT SHEET April 14, 2003 (http://www.epa.gov/opptintr/pfoa/pfoafacts.pdf) announced that a "telomer" may have possibility to form PFOA due to its metabolism or decomposition. It is also announced that the "telomer" has been used in a large number of commercial products including fire fighting foams, care products and cleaning products as well as water- and oil-repelling coatings and

antifouling coatings on carpets, textiles, paper and leather.

Disclosure of the Invention

Problems to be Solved by the Invention

[0007]

An object of the present invention is to provide a surface treatment agent having excellent water- and oil-repellency and antifouling property, even if the fluoroalkyl group in a fluorine-containing polymer has 6 or less carbon atoms.

Means for Solving the Problems

[0008]

The present invention provides a surface treatment agent comprising a fluorine-containing polymer, and water and/or an organic solvent, wherein the fluorine-containing polymer comprises repeating units derived from a fluorine-containing monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

[wherein X is a hydrogen atom or a methyl group;

Y is -O- or -NH-;

Z is -S- or $-SO_2-$;

Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and

m is from 1 to 10, n is from 0 to 10, and p is 0 or 1].

The present invention provides (a) a fluorine-containing monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

[wherein X is a hydrogen atom or a methyl group;

Y is -O- or -NH-;

Z is -S-;

Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and

m is from 1 to 10, n is from 0 to 10, and p is 0 or 1,

provided that when p is 0, Y is -NH-, and that when p is 1, Y is -O- and n is 0].

The present invention provides a fluorine-containing polymer comprising (A) repeating units derived from the above-mentioned fluorine-containing monomer (a).

Effect of the Invention

[0009]

According to the present invention, there is provided a surface treatment agent excellent in water repellency, water repellency and antifouling property.

Best Modes for Carrying out the Invention

[0010]

The surface treatment agent of the present invention comprises (A) a fluorine-containing polymer which comprises repeating units derived from (a) a fluorine-containing monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

[wherein X is a hydrogen atom or a methyl group;

Y is -O- or -NH-;

Z is -S- or $-SO_2-$;

Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and

m is from 1 to 10, n is from 0 to 10, and p is 0 or 1].

That is, the fluorine-containing polymer forming the surface treatment agent comprises repeating units (A) derived from the above-mentioned fluorine-containing monomer (a).

The fluorine-containing polymer is a homopolymer or a copolymer.

When the fluorine-containing polymer is a copolymer, the fluorine-containing polymer may contain

(B) repeating units derived from a monomer free from a

fluorine atom, and

(C) optionally, repeating units derived from a crosslinkable monomer,

in addition to the repeating unit (A).

[0011]

In the present invention, the repeating unit (A) is formed by the fluorine-containing monomer (a) of the formula (I).

[0012]

In the above-mentioned formula, the Rf group is preferably a perfluoroalkyl group. The number of carbon atom in the Rf group is from 1 to 6, for example, from 1 to 4. Examples of the Rf group are $-CF_3$, $-CF_2CF_3$, $-CF_2CF_2CF_3$, $-CF(CF_3)_2$, $-CF_2CF_2CF_2CF_3$, $-CF_2CF(CF_3)_2$, $-C(CF_3)_3$, $-(CF_2)_4CF_3$, $-(CF_2)_2CF(CF_3)_2$, $-CF_2C(CF_3)_3$, $-CF(CF_3)CF_2CF_2CF_3$, $-(CF_2)_5CF_3$, $-(CF_2)_3CF(CF_3)_2$, $-(CF_2)_4CF(CF_3)_2$ and the like.

In the formula, m may be, for example, from 2 to 10, and n may be, for example, from 1 to 10.

Preferably, p is 1, when Y is -O-, and p is 0, when Y is -NH-.

Examples of the fluorine-containing monomer (a) include the following:

[0013]

$CH_2=C(-X)-C(=O)-O-(CH_2)_m-S-(CH_2)_n-Rf$

$CH_2=C(-X)-C(=O)-O-(CH_2)_m-SO_2-(CH_2)_n-Rf$

$CH_2=C(-X)-C(=O)-NH-(CH_2)_n-Rf$

[wherein X is a hydrogen atom or a methyl group;
Rf is a fluoroalkyl group having 1 to 6 carbon atoms; and
m is from 1 to 10, and n is from 0 to 10].

[0014]

Specific examples of the fluorine-containing monomer (a) include the following:

$CH_2=CH-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=CH-C(=O)-NH-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-SO_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-NH-(CH_2)_2-Rf$

[0015]

$CH_2=CH-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=CH-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CH_3)-C(=O)-O-(CH_2)_3-SO_2-(CH_2)_2-Rf$

[wherein Rf is a fluoroalkyl group having 1 to 6 carbon atoms].

[0016]

The following fluorine-containing monomers are novel compounds:

$CH_2=C(-X)-C(=O)-O-(CH_2)_m-S-Rf$ (1)

$CH_2=C(-X)-C(=O)-NH-(CH_2)_n-Rf$ (2)

[wherein m is from 1 to 10, and n is from 0 to 10].

The fluorine-containing monomers (1) and (2) are prepared, for example, as follows.

[0017]

Fluorine-Containing Monomer (1)

Mercaptoethanol is reacted with perfluoroalkyl iodide having a Rf group which has one end substituted with iodine, in a solvent (for example, water/DMF), for example, at 30 to 90°C for 0.5 to 30 hours, to give a perfluoroalkyl thioethanol. This alcohol is reacted with acrylic acid in a solvent (for example, cyclohexane) in the presence of a catalyst (for example, paratoluene sulfonic acid), for example, at 30 to 70°C for 0.5 to 30 hours to give perfluoroalkylthioethyl acrylate.

[0018]

Fluorine-Containing Monomer (2)

Into a reactor, tridecylmethyl ammonium chloride, perfluoroalkylethyl iodide having a Rf group which is substituted at one end with iodine, and an aqueous solution of sodium azide are added (for example, at room temperature), and they are reacted under stirring and heating (for example, at 50 to 95°C, particularly at 90°C) for 1 to 50 hours (for example, 20 hours). After completion of the reaction, the disappearance of the raw material, that is, the iodine compound is confirmed by GC (gas chromatography). The reaction liquid is cooled to room temperature (23°C), and the lower organic layer is separated. The aqueous layer is extracted with diisopropyl ether, and the extract as such is used in the next reaction.

Into an autoclave, the reaction extract and a catalyst (for example, 10% palladium/carbon) are added, and then, a hydrogen gas (for example, at a pressure of 2 to 15 Kg/cm^2, particularly 8 Kg/cm^2) is charged therein. The mixture is stirred, for example, at 10 to 30°C (particularly room

temperature (23°C)) for 1 to 30 hours (for example, 15 hours). The disappearance of the raw material is confirmed by GC, and the organic layer is filtered by celite. After that, the filtrate as such is used in the next reaction.

Into a flask, triethylamine and 4-t-butyl catechol are added to the solution of the amino product in diisopropyl ether under cooling with ice. Then, acrylic acid chloride is dropwise added under cooling with ice, and the mixture is stirred at room temperature (23°C) for 0.5 to 50 hours (for example, 12.5 hours). The produced solid is filtered, and the filtrate is washed with a 5% aqueous solution of citric acid, and the organic layer is dried over magnesium sulfate. The organic layer is filtered, and the filtrate is concentrated under reduced pressure. The residue is subjected to silica gel chromatography to give perfluoroalkylethylacrylic acid amide.

[0019]

The repeating units (B) are derived from the monomer (b) free from a fluorine atom. The monomer (b) is preferably a fluorine-free monomer having a carbon-carbon double bond. The monomer (b) is preferably a vinyl monomer which is free from fluorine. The fluorine atom-free monomer (b) is generally a compound having one carbon-carbon double bond. Preferable examples of the fluorine atom-free monomer (b) include, for example, ethylene, vinyl acetate, vinyl halide (for example, vinyl chloride) vinylidene halide (for example, vinylidene chloride), acrylonitrile, styrene, polyethyleneglycol (meth)acrylate, polypropyleneglycol (meth)acrylate, methoxypolyethylene-glycol (meth)acrylate, methoxypolypropyleneglycol (meth)acrylate, vinyl alkyl ether and isoprene. The

fluorine atom-free monomer (b) is not limited to these examples.

[0020]

The fluorine atom-free monomer (b) may be a (meth)acrylate ester having an alkyl group. The number of carbon atoms in the alkyl group may be from 1 to 30, for example, from 6 to 30, e.g., from 10 to 30. For example, the fluorine atom-free monomer (b) may be an acrylate of the general formula:

$CH_2=CA^1COOA^2$

[wherein A^1 is a hydrogen atom or a methyl group, and A^2 is an alkyl group represented by C_nH_{2n+1} (n = 1 to 30)].

[0021]

The repeating units (C) are derived from the crosslinkable monomer (c). The crosslinkable monomer (c) may be a fluorine-free compound having at least two reactive groups and/or carbon-carbon double bonds. The crosslinkable monomer (c) may be a compound having at least two carbon-carbon double bonds, or a compound having at least one carbon-carbon double bond and at least one reactive group. Examples of the reactive group include a hydroxyl group, an epoxy group, a chloromethyl group, a blocked isocyanate group, an amino group and a carboxyl group.

[0022]

Examples of the crosslinkable monomer (c) include diacetoneacrylamide, (meth)acrylamide, N-methylolacrylamide, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, butadiene, chloroprene and glycidyl

(meth)acrylate, to which the crosslinkable monomer is not limited.

[0023]

The copolymerization with the monomer (b) and/or the monomer (c) makes it possible to improve various properties of the polymer such as water- and oil-repellency and antifouling property; cleaning durability and washing durability of these properties; solubility in a solvent; hardness; and feeling.

[0024]

In the fluorine-containing polymer, the amount of the fluorine atom-free monomer (b) may be from 0 to 500 parts by weight, for example, from 0.1 to 100 parts by weight, particularly from 0.1 to 50 parts by weight, and the amount of the crosslinkable monomer (c) may be from 0 to 50 parts by weight, for example, from 0 to 20 parts by weight, particularly from 0.1 to 15 parts by weight, based on 100 parts by weight of the fluorine-containing monomer (a).

[0025]

The fluorine-containing polymer can be produced as follows.

In case of solution polymerization, there is exemplified a method of dissolving the monomer(s) in an organic solvent in the presence of a polymerization initiator, displacing the inner atmosphere with nitrogen, and stirring the solution under heating at a temperature of from 30 to 120°C for 1 to 10 hours. Examples of the polymerization initiator include azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate and

diisopropyl peroxydicarbonate. The polymerization initiator may be used in an amount of from 0.01 to 20 parts by weight, for example, from 0.01 to 10 parts by weight, based on 100 parts by weight of the monomer(s).

[0026]

The organic solvent is inert to the monomer(s) and dissolves the monomer(s). Examples thereof include acetone, chloroform, HCHC225, isopropyl alcohol, pentane, hexane, heptane, octane, cyclohexane, benzene, toluene, xylene, petroleum ether, tetrahydrofuran, 1,4-dioxane, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, tetrachlorodifluoroethane and trichlorotrifluoroethane. The organic solvent may be used in an amount of from 50 to 2,000 parts by weight, for example, from 50 to 1,000 parts by weight, based on total 100 parts by weight of the monomers.

[0027]

In case of emulsion polymerization, there can be employed a method of emulsifying the monomers in water in the presence of a polymerization initiator and an emulsifying agent, displacing the inner atmosphere with nitrogen, and copolymerizing the emulsion under stirring, for example, at a temperature of from 50 to 80°C for 1 to 10 hours. Examples of the polymerization initiator include water-soluble initiators (e.g., benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, 1-hydroxycyclohexyl hydroperoxide, 3-carboxypropionyl peroxide, acetyl peroxide, azobisisobutylamidine dihydrochloride, azobisisobutyronitrile, sodium peroxide, potassium

persulfate and ammonium persulfate) and oil-soluble initiators (e.g., azobisisobutyronitrile, benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate and diisopropyl peroxydicarbonate). The polymerization initiator may be used in an amount of from 0.01 to 10 parts by weight based on 100 parts by weight of the monomers.

[0028]

In order to obtain a copolymer dispersion in water, which is superior in storage stability, it is desirable that the monomers are atomized in water by using an emulsifying device capable of applying a strong shattering energy (e.g., a high-pressure homogenizer and an ultrasonic homogenizer), and are then polymerized in the presence of an oil-soluble polymerization initiator. As the emulsifying agent, any of various emulsifying agents such as anionic, cationic and nonionic emulsifying agents can be used in an amount of from 0.5 to 20 parts by weight based on 100 parts by weight of the monomers. An anionic and/or nonionic and/or cationic emulsifying agent is preferably used. When the monomers are not completely compatibilized, preferably, a compatibilizing agent (e.g., a water-soluble organic solvent and a low-molecular weight monomer) capable of sufficiently compatibilizing the monomers is added to these monomers. By the addition of the compatibilizing agent, the emulsifiability and polymerizability can be improved.

[0029]

Examples of the water-soluble organic solvent include acetone, methyl ethyl ketone, ethyl acetate, propylene glycol, dipropylene glycol monomethyl ether, dipropylene

glycol, tripropylene glycol and ethanol. The water-soluble organic solvent may be used in an amount of from 1 to 50 parts by weight, e.g., from 10 to 40 parts by weight, based on 100 parts by weight of water. Examples of the low-molecular weight monomer include methyl methacrylate, glycidyl methacrylate and 2,2,2-trifluoroethyl methacrylate. The low-molecular weight monomer may be used in an amount of from 1 to 50 parts by weight, e.g., from 10 to 40 parts by weight, based on total 100 parts by weight of the monomers.

[0030]

The surface treatment agent of the present invention is preferably in the form of a solution, an emulsion or an aerosol. The surface treatment agent comprises the fluorine-containing polymer and a medium (particularly a liquid medium such as an organic solvent and/or water). The concentration of the fluorine-containing polymer in the surface treatment agent may be, for example, from 0.01 to 50 % by weight.

[0031]

The surface treatment agent of the present invention can be applied to a subject material by a known method. Usually, the surface treatment agent is diluted with or dispersed in an organic solvent or water, and is adhered to surfaces of the subject material by a well-known method such as immersion coating, spray coating or foam coating, and is then dried. If necessary, the surface treatment agent is applied together with a suitable crosslinking agent, followed by curing. It is also possible to add other surface treatment agent (for example, a water repellent or an oil repellent), a mothproofing agent, a

softener, an antimicrobial agent, a flame retardant, an antistatic agent, a paint fixing agent, a crease-proofing agent, etc. to the surface treatment agent of the present invention. In case of the immersion coating, the concentration of the fluorine-containing polymer in the treatment liquid may be from 0.05 to 10% by weight. In case of the spray coating, the concentration of the fluorine-containing polymer in the treatment liquid may be from 0.1 to 5% by weight. A stain blocker may be used. When the stain blocker is used, it is preferable to use an anionic or nonionic emulsifying agent.

[0032]

Examples of the subject material to be treated with the surface treatment agent (for example, a water- and oil-repellent) of the present invention include a textile, masonry, a filter (for example, an electrostatic filter), a dust protective mask, components of fuel cell (for example, a gaseous diffusion electrode and a gaseous diffusion support), glass, paper, wood, leather, fur, asbestos, brick, cement, metal and oxide, ceramics, plastics, a coated surface and a plaster. The textile may be particularly a carpet. As the textile, various examples are given. Examples of the textile include animal- or vegetable-origin natural fibers such as cotton, hemp, wool and silk; synthetic fibers such as polyamide, polyester, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride and polypropylene; semi-synthetic fibers such as rayon and acetate; inorganic fibers such as glass fiber, carbon fiber and asbestos fiber; and a mixture of these fibers. The treatment agent of the present invention can be suitably used for carpets made from nylon and polypropylene.

[0033]

The textile may be any of a fiber, a yarn, a fabric, etc. When a carpet is treated with the surface treatment agent of the present invention, the carpet may be made after fibers or yarns have been treated with the surface treatment agent, or a finished carpet may be treated with the surface treatment agent.

Examples

[0034]

Examples of the present invention are specifically illustrated but are not to be construed to limit the scope of the invention in any way.

The evaluation tests were conducted as follows.

Shower Water Repellency Test

The shower water repellency is expressed by water repellency No. (see Table 1 below) evaluated by the spray method according to JIS-L-1092.

[0035]

[Table 1]

Table 1

Water repellency No.	State
5	No water droplet adhering to or wetting the surface of a fabric
4	Water droplets slightly adhering to or wetting the surface of a fabric
3	Water droplets partially wetting the surface of a fabric
2	Water droplets wetting the surface of a fabric
1	Water droplets entirely wetting the surface of a fabric

[0036]

Water-Repellency Test

A test piece of a treated fabric is stored in a thermo-hygrostat controlled at a temperature of 21°C and a humidity of 65% for at least 4 hours. Test liquids (isopropyl alcohol (IPA), water and a mixture thereof, shown in Table 2) which have been stored at 21°C are used. The test is conducted in an air-conditioned room controlled at a temperature of 21°C and a humidity of 65%. The test liquid in an amount of 0.05 ml is gently dropped on the test piece, and the test piece is left to stand for 30 seconds. If some droplets of the test liquid remain on the test piece, this test liquid is regarded as passing the test. The water-repellency of the test liquid is expressed

by a point corresponding to a maximum content (% by volume) of isopropyl alcohol (IPA) in the test liquid which passes the test. The water-repellency is evaluated in twelve levels of Fail, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 in the order of an inferior level to a superior level.

[0037]

[Table 2]

Table 2 Water-Repellency Test Liquid

Point	(% by volume)	
	Isopropyl alcohol	Water
10	100	0
9	90	10
8	80	20
7	70	30
6	60	40
5	50	50
4	40	60
3	30	70
2	20	80
1	10	90
0	0	100
Fail	Inferior to isopropyl alcohol 0/water 100	

[0038]

Oil-Repellency Test

A test piece of a treated fabric is stored in a thermo-hygrostat controlled at a temperature of 21°C and a humidity of 65% for at least 4 hours. Test liquids (shown in Table 3) stored at 21°C are used. The test is conducted

in an air-conditioned room controlled at a temperature of 21°C and a humidity of 65%. The test liquid in an amount of 0.05 ml is gently dropped on the test piece, and the test piece is left to stand for 30 seconds. If some droplets remain on the test piece, this test liquid is regarded as passing the test. The oil-repellency of the test liquid is expressed by a maximum point of the test liquid which passes the test. The oil-repellency is evaluated in nine levels of Fail, 1, 2, 3, 4, 5, 6, 7 and 8 in the order of an inferior level to a superior level.

[0039]

[Table 3]

Table 3 Oil-Repellency Test Liquid

Point	Test liquid	Surface tension (dyne/cm, 25°C)
8	n-Heptane	20.0
7	n-Octane	21.8
6	n-Decane	23.5
5	n-Dodecane	25.0
4	n-Tetradecane	26.7
3	n-Hexadecane	27.3
2	Mixture liquid of n-Hexadecane 35/nujol 65	29.6
1	Nujol	31.2
Fail	Inferior to 1	-

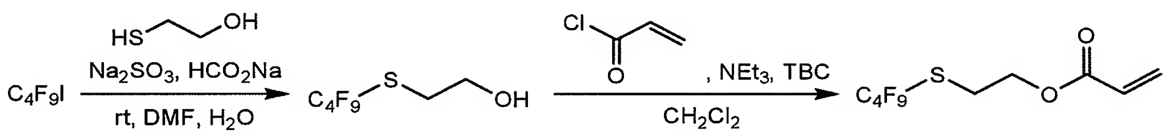
[0040]

Monomers are synthesized as follows:

Synthetic Example 1 (9FSEA monomer)

Synthesis of 2-(perfluorobutylthio)ethyl acrylate

[Chemical Formula 1]



[0041]

1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (138.4 g (400 mmol)) was dissolved in a mixture liquid of DMF (400 ml) and water (80 ml), and mercaptoethanol (32.2g (400 mmol)) was added. Further, sodium formate (27.2g (400 mmol)), sodium sulfite heptahydrate (100.9 g (400 mmol)) were added, and the mixture was stirred at room temperature (23°C) for one night. Water (1 L) and isopropyl ether (1 L) were added to the reaction liquid, which was then separated. The resulting aqueous layer was further extracted with isopropyl ether (500 ml x 2). The organic layer was washed with 10% hydrochloric acid (500 ml), water (500 ml) and a saturated saline solution (500 ml), dried over anhydrous magnesium sulfate and filtered. The solvent was distilled off from the organic layer. A solution of a part (25.9 g, equivalent to 78 mmol) of the condensate [2-(perfluorosulfonyl)ethanol], triethylamine (19.5 g (140 mmol)) and 4-t-butylcatechol (one particle) in dichloromethane (200 ml) was cooled to 0°C. Acryloyl chloride (8.5 ml (10.5 mmol)) was slowly added dropwise (the internal temperature raised to 15°C). After removing from the ice bath, the mixture was stirred at room temperature (23 °C) for 1 hour, and the disappearance of the raw material was confirmed by GC. The reaction liquid was washed with a 5% aqueous citric acid, and dried over anhydrous magnesium sulfate. The reaction liquid was then

filtered and the solvent was distilled off therefrom. A fraction of 65 to 67°C /4 mmHg was collected by vacuum distillation to give acrylate ester (23.6 g). Yield: 86.4%.

[0042]

^{1}H NMR($CDCl_3$; internal standard TMS δppm): 6.46(dd, 1H, J_{AB}=1.6Hz, J_{AX}=17.2Hz, $C\underline{H_A}H_B$=C), 6.14(dd, 1H, J_{AX}=17.2Hz, J_{BX}=10.3Hz, C=$C\underline{H_X}$), 5.90(dd, 1H, J_{BX}=10.3Hz, J_{AB}=1.6Hz, $CH_A\underline{H_B}$=C), 4.40(t, 2H, J_{HH}=6.4Hz, $O\underline{CH_2}$), 3.23(t, 2H, J_{HH}=6.4Hz, $\underline{CH_2}S$)

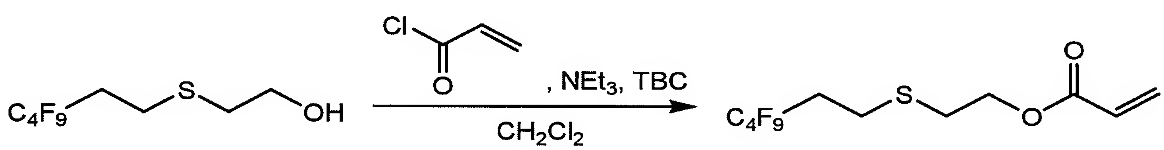
^{19}F NMR($CDCl_3$; internal standard $CFCl_3$ δppm): -81.5(m, 3F, CF_3), -87.8(m, 2F, CF_2S), -121.2(m, 2F, CF_2), -126.0(m, 2F, CF_2).

[0043]

Synthetic Example 2 (9FESEA monomer)

Synthesis of 2-(3,3,4,4,5,5,6,6,6-nonafluorohexylthio)ethyl acrylate

[Chemical formula 2]



[0044]

A solution of 2-(3,3,4,4,5,5,6,6,6-nonafluorohexylthio)ethanol (81 g (250 mmol)), triethylamine (52.3 ml (375 mmol)), 4-t-butylcatechol (one particle) in dichloromethane (500 ml) was cooled to 0°C, and acryloyl chloride (24.4 ml (300 mmol)) was slowly added dropwise in 10 minutes. The mixture was stirred at room temperature (23°C) for 40 minutes. The reaction liquid was washed with a 5% aqueous citric acid (500 ml) and a saturated saline solution, and dried over anhydrous magnesium sulfate. The reaction liquid was filtered to

give a crude acrylate ester (81.0 g). Yield: 85.7%.

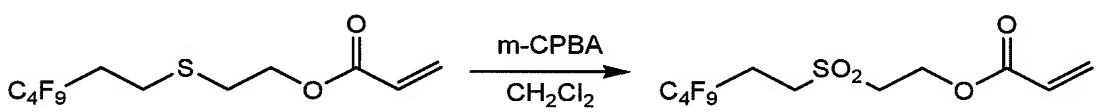
^{1}H NMR($CDCl_3$; internal standard TMS δppm): 6.45(dd, 1H, J_{AB}=1.2Hz, J_{AX}=17.2Hz, $C\underline{H_A}H_B$=C), 6.14(dd, 1H, J_{AX}=17.2Hz, J_{BX}=10.3Hz, C=$C\underline{H_X}$), 5.88(dd, 1H, J_{BX}=10.3Hz, J_{AB}=1.2Hz, $CH_A\underline{H_B}$=C), 4.36(t, 2H, J_{HH}=6.6Hz, $O\underline{CH_2}$), 2.8(m, 4H, $C\underline{H_2}SC\underline{H_2}$), 2.4(m, 2H, $C\underline{H_2}CF_2$)

^{19}F NMR($CDCl_3$; internal standard $CFCl_3$ δppm): -81.5(m, 3F, CF_3), -115.0(m, 2F, CF_2), -124.8(m, 2F, CF_2), -126.5(m, 2F, CF_2).

[0045]

Synthetic Example 3 (9FESO2EA monomer)

Synthesis of 2-(3,3,4,4,5,5,6,6,6-nonafluorohexyl-sulfonyl)ethyl acrylate



[0046]

A solution of crude 2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexylthio)ethyl acrylate (81.0 g (214 mmol)) prepared in Synthetic Example 2 in dichloromethane (1.5 L) was cooled with ice, and m-chloroperbenzoic acid (100 g (446 mmol)) was gradually added. After completion of the addition, the mixture was stirred at room temperature (23°C) for one night, filtered and washed. The resulting filtrate was washed with a 30% aqueous solution of sodium thiosulfate pentahydrate. After the disappearance of peracid in the aqueous layer was confirmed by a iodine/starch reaction, the organic layer was washed with a saturated aqueous sodium dicarbonate. The organic layer was dried over magnesium sulfate and filtered. The resulting filtrate was condensed under reduced pressure, and the residue was purified by silica gel chromatography (n-hexane:ethyl

acetate = 5:1). The white solid obtained after the condensation was dried to give a sulfone substance (55.4 g). Yield: 63.1%.

^{1}H NMR($CDCl_3$; internal standard TMS δppm): 6.45(dd, 1H, J_{AB}=1.1Hz, J_{AX}=17.3Hz, $C\underline{H_A}H_B$=C), 6.12(dd, 1H, J_{AX}=17.3Hz, J_{BX}=10.5Hz, C=$C\underline{H_X}$), 5.95(dd, 1H, J_{BX}=10.5Hz, J_{AB}=1.1Hz, $CH_A\underline{H_B}$=C), 4.65(t, 2H, J_{HH}=5.6Hz, $OC\underline{H_2}$), 3.42(t, 2H, J_{HH}=5.7Hz, $C\underline{H_2}SO_2$), 3.33(tt, 2H, J_{HH}=8.5Hz, $SO_2C\underline{H_2}CH_2CF_2$), 2.69(m, 2H, $C\underline{H_2}CF_2$)

^{19}F NMR($CDCl_3$; internal standard $CFCl_3$ δppm): -81.5(t, 3F, J=9.3Hz, CF_3), -114.4(m, 2F, CF_2), -124.6(m, 2F, CF_2), -126.5(m, 2F, CF_2).

[0047]

Polymers were synthesized as follows:

Preparative Example 1

9FSEA homopolymer

Into a 200 mL four-necked flask, the monomer (9FSEA monomer) (10 g (0.029 mol)) prepared in Synthetic Example 1 and butyl acetate (27 g) were charged, and nitrogen was allowed to flow for 60 minutes. The inner temperature was raised to 60°C, and then, Perbutyl PV (0.11 g (0.0006 mol)) dissolved in butyl acetate (1 g) was added, and the mixture was reacted for 8 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white starch syrup-like precipitate. The supernatant liquid was removed by decantation, and the solvent was distilled off by setting the precipitate in an evaporator. Thus, a very highly viscous and transparent

liquid substance (6.7 g) (Polymer yield 67%) was obtained. The polymer was identified by elemental analysis (Table 4).

[0048]

Preparative Example 2

9FESEA homopolymer

Into a 200 mL four-necked flask, the monomer (9FESEA monomer) (10 g (0.026 mol)) prepared in Synthetic Example 2 and butyl acetate (27 g) were charged, and nitrogen was allowed to flow for 60 minutes. The inner temperature was raised to 60°C, and Perbutyl PV (0.11 g (0.0006 mol)) dissolved in butyl acetate (1 g) was added. The mixture was reacted for 6 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white starch syrup-like precipitate. The supernatant liquid was removed by decantation, and the solvent was distilled off by setting the precipitate in an evaporator. Thus, a very highly viscous and transparent liquid substance (6.2 g) (Polymer yield 62%) was obtained. The polymer was identified by elemental analysis (Table 4).

[0049]

Preparative Example 3

9FESEA/StA copolymer

Into a 200 mL four-necked flask, the monomer (9FESEA monomer) (7 g (0.02 mol)) prepared in Synthetic Example 2, stearyl acrylate (3 g (0.0093 mol)) and butyl acetate (27 g) were charged, and nitrogen was allowed to flow for 60 minutes. The inner temperature was raised to 60°C, and then, Perbutyl PV (0.11 g (0.0006 mol)) dissolved in butyl

acetate (1 g) was added, and the mixture was reacted for 4 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white starch syrup-like precipitate. The supernatant liquid was removed by decantation, and the solvent was distilled off by setting the precipitate in an evaporator. Thus, a very highly viscous and white liquid substance (9.9 g) (Polymer yield 99%) was obtained. The polymer was identified by elemental analysis (Table 4).

[0050]

Preparative Example 4

9FESO2EA homopolymer

Into a 200 mL four-necked flask, the monomer (9FESO2EA) (7 g (0.017 mol)) prepared in Synthetic Example 3 and butyl acetate (21 g) were charged, and nitrogen was allowed to flow for 60 minutes. The inner temperature was raised to 60°C, and then, Perbutyl PV (0.11 g (0.0006 mol)) dissolved in butyl acetate (1 g) was added, and the mixture was reacted for 5 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white precipitate. This white precipitate was filtered under reduced pressure and dried in a vacuum desiccator to give a white powder (6.8 g) (Polymer yield 97%). The polymer was identified by elemental analysis (Table 4).

[0051]

Preparative Example 5

<u>9FESO2EA/StA copolymer</u>

Into a 200 mL four-necked flask, the monomer (9FESO2EA) (3 g (0.0073 mol)) prepared in Synthetic Example 3, stearyl acrylate (1.26 g (0.0039 mol) and butyl acetate (12 g) were charged, and nitrogen was allowed to flow for 60 minutes. The inner temperature was raised to 60°C, and then, Perbutyl PV (0.032 g (0.002 mol)) dissolved in butyl acetate (0.4 g) was added, and the mixture was reacted for 7 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white precipitate. This white precipitate was filtered under reduced pressure and dried in a vacuum desiccator to give a white powder (3.8 g) (Polymer yield 91%). The polymer was identified by elemental analysis (Table 4).

[0052]

Comparative Preparative Example 1

<u>9FA homopolymer</u>

Into a 200 mL four-necked flask, 2-(perfluorobutyl)ethyl acrylate (9F-Alc/AA) (R-1420 manufactured by Daikin Chemical Sales, Ltd.) (15 g (0.047 mol)) and tetrachlorohexafluorobutane (121 g) were charged. The solution was bubbled with nitrogen for 30 minutes, and then, the nitrogen in the gas phase was displaced for 30 minutes. The inner temperature was raised to 60°C, and Perbutyl PV (1.61 g (0.0092 mol)) dissolved in trichloroethane (7.86 g) was added. The mixture was

reacted for 5.5 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of monomer peaks was confirmed to determine the termination of the reaction. After completion of the reaction, methanol was added to the polymerized solution to settle a white starch syrup-like precipitate. The supernatant liquid was removed by decantation, and the solvent was distilled off by setting the precipitate in an evaporator. Thus, a very highly viscous and transparent liquid substance (9.36 g) (Polymer yield 82%) was obtained. The polymer was identified by elemental analysis (Table 4).

[0053]

Comparative Preparative Example 2

<u>9FA/StA copolymer</u>

Into a 100 mL four-necked flask, 2-(perfluorobutyl)ethyl acrylate (9F-Alc/AA) (R-1420 manufactured by Daikin Chemical Sales, Ltd.) (7.00 g (0.022 mol)) and tetrachlorohexafluorobutane (56.47 g) were charged. The solution was bubbled with nitrogen for 30 minutes, and then, the nitrogen in the gas phase was displaced for 30 minutes. The inner temperature was raised to 60°C, and then, Perbutyl PV (0.75 g (0.0043 mol)) dissolved in trichloroethane (3.67 g) was added. The mixture was reacted for 6 hours. The step control in the reaction was conducted on the basis of gas chromatography, and the disappearance of the 9F-Alc/AA and stearyl acrylate monomer peaks was confirmed to determine the termination of the reaction. After completion of reaction, methanol was added to the polymerized solution to give a white precipitate. The supernatant liquid was removed by decantation, and the solvent was distilled off by setting

the precipitate in an evaporator. Thus, a very highly viscous and white opaque liquid substance (7.06 g) (Polymer yield 70.6%) was obtained. The polymer was identified by elemental analysis (Table 4).

[0054]

Example 1

The polymer (1.5 g) obtained in Preparative Example 1 was dissolved in HCFC-225 (150 g). After one sheet of nylon test fabric (510 mm × 205 mm) was immersed in this test solution (150 g) for about 5 minutes, the solvent was removed, using a centrifugal dehydrator (500 rpm, 30 seconds). The same operation was conducted on each one sheet of PET test fabric (510 mm × 205 mm), PET/cotton mixture test fabric (510 mm × 205 mm) and cotton test fabric (510 mm × 205 mm). After that, each of the test fabrics was dried at 28°C for one night.

[0055]

Next, each one sheet of the nylon test fabric, the PET test fabric, the PET/cotton mixture test fabric and the cotton test fabric was treated with a pin tenter at 150°C for 3 minutes, and each of the test fabrics was cut into halves (255 mm × 205 mm). One half was used for a shower water repellency test, and the other half was used for a water repellency test and an oil repellency test. The test results are shown in Table 5.

[0056]

Example 2

The polymer obtained in Preparative Example 2 was treated in the same manner as in Example 1. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test

results are shown in Table 5.

[0057]

Example 3

The polymer obtained in Preparative Example 3 was treated in the same manner as in Example 1. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test results are shown in Table 5.

[0058]

Example 4

The polymer obtained in Preparative Example 4 was treated in the same manner as in Example 1, except that the solvent was changed to butyl acetate. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test results are shown in Table 5.

[0059]

Example 5

The polymer obtained in Preparative Example 5 was treated in the same manner as in Example 1. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test results are shown in Table 5.

[0060]

Comparative Example 1

The polymer obtained in Comparative Preparative Example 1 was treated in the same manner as in Example 1, except that the solvent was changed to HCFC-225. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test results are shown in Table 5.

[0061]

Comparative Example 2

The polymer obtained in Comparative Preparative Example 2 was treated in the same manner as in Example 1, except that the solvent was changed to HCFC-225. Then, the test fabrics were subjected to shower water repellency tests, water repellency tests and oil repellency tests. The test results are shown in Table 5.

[0062]

[Table 4]

Elemental Analysis	F		C		H		N		Cl	
	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
Preparative Example 1	46.85	48.77	31.02	30.83	2.31	2.16	0.00	0.00	0.00	0.00
Preparative Example 2	43.68	45.12	34.77	34.86	3.18	3.13	0.00	0.00	0.00	0.00
Preparative Example 3	28.65	31.50	46.98	47.59	5.71	6.17	0.00	0.00	0.00	0.00
Preparative Example 4	39.92	41.61	32.20	32.15	2.77	2.89	0.00	0.00	0.00	0.00
Preparative Example 5	28.35	29.22	45.92	45.50	5.52	5.96	0.00	0.00	0.00	0.00
Comparative Preparative Example 1	49.43	53.77	33.11	33.96	2.47	2.20	0.00	0.00	0.00	0.00
Comparative Preparative Example 2	35.91	37.64	48.06	47.11	4.84	5.24	0.00	0.00	0.00	0.00

[0063]

[Table 5]

Table 5

Example 1			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	70	3	3
PET	80	3	3
PET/ Cotton	50	3	3
Cotton	50	3	3

Example 3			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	70	3	2
PET	80	4	3
PET/ Cotton	50	3	3
Cotton	50	3	3

Example 2			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	70	3	3
PET	80	3	3
PET/ Cotton	50	3	3
Cotton	0	3	3

Example 5			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	100	9	6
PET	80	5	6
PET/ Cotton	80	4	6
Cotton	80	3	6

Example 4			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	100	4	3
PET	100	4	3
PET/ Cotton	80	4	3
Cotton	70	7	3

Comparative Example 1			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	50	3	0
PET	70	3	3
PET/ Cotton	0	3	3
Cotton	0	Fail	3

Comparative Example 2			
Test fabric	Shower water repellency	Water repellency	Oil repellency
Nylon	70	4	2
PET	50	4	3
PET/ Cotton	50	4	2
Cotton	0	4	2

Document Name: Abstract

Summary:

Purpose: To provide a surface treatment agent having excellent water repellency, oil repellency and antifouling property.

Solution: A surface treatment agent comprising a fluorine-containing polymer which comprises

(A) repeating units derived from a fluorine-containing monomer of the formula:

$$CH_2=C(-X)-C(=O)-Y-[-(CH_2)_m-Z-]_p-(CH_2)_n-Rf \qquad (I)$$

(wherein X is a hydrogen atom or a methyl group);

(B) optionally, repeating units derived from a fluorine-free monomer; and

(C) optionally, repeating units derived from a crosslinkable monomer.

Selected Figure: Nil